

Vapor-liquid equilibria of alternative refrigerants and their binaries by molecular simulations

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Abstract

Alternative refrigerants HFC125 (CHF_2CF_3), HFC 134a ($\text{CF}_3\text{CH}_2\text{F}$) are modeled as a dipolar two-center Lennard-Jones fluid and alternative refrigerant HFC32 (CH_2F_2) is modeled as a dipolar Lennard-Jones fluid. We calculate vapor-liquid equilibria of these refrigerants by Gibbs-Duhem integration and vapor-liquid equilibria of two binaries (HFC 125+HFC 134a, and HFC 134a+HFC 32) by the reaction Gibbs ensemble Monte Carlo method. Potential parameters of the model are fitted to the critical temperature and vapor-liquid equilibrium data. The predictions are very good, and of comparable accuracy to those obtained using the Wilson and the UNIFAC thermodynamic-based approaches, even though such approaches use experimental mixture information.

Keywords: alternative refrigerants, mixtures, vapor-liquid equilibria and molecular simulations

1. Introduction

Vapor-liquid equilibrium (VLE) calculations in chemistry and chemical engineering are traditionally carried out by means of empirically based thermodynamic equation of state (EOS) and/or liquid-state activity-coefficient models [1, 2]. The main goal of such calculations is the prediction of the $PTxy$ behavior of the mixture (where P is the system pressure, T the temperature, and x and y denote the compositions of the coexisting phases). To implement these approaches, one requires as input information accurate data concerning the vapor pressure behavior of each constituent pure fluid. These data are then combined with the mixture model; in addition, a mixture parameter appearing in the theory is often evaluated by means of an experimental measurement on the mixture. Given this input information, the system behavior is then calculated using standard thermodynamic relations [2]. The accuracy of these approaches in predicting the experimental data varies; as with all empirically based methods, the path to further progress is not always clear. An alternative, and much less well-developed approach, uses as input a molecular-based intermolecular potential model for the species and their interactions. The properties of the mixture are then calculated by computer simulation, using the Gibbs ensemble Monte Carlo

(GEMC) method [3], the constant pressure-constant temperature (NPT) + test particle method [4], and/or the Gibbs-Duhem integration method [5]. Molecular-based simulation approaches have considerable advantage over the empirically based approaches that predictions may be made in the absence of experimental data of any kind, provided one could construct an intermolecular potential model for the system. The construction of reasonably accurate such models is now a relatively straightforward task [6]. Similarly, the computer simulation approaches can also calculate the volumetric properties of the mixture, which are often difficult to determine experimentally. However, the accuracy of these approaches for the calculation of phase equilibria has generally been inferior to results obtained from the empirically based methods, especially for mixtures of any degree of complexity [7]. This is illustrated by the results of De Pablo and Prausnitz [8], and De Pablo et al. [9], who applied the GEMC approach to binary alkane mixtures, of Götlib et al. [10], Agrawal and Wallis [11], and Strauch and Cummings [12], who applied the GEMC approach to binary mixtures of methanol + ethane, methanethiol +propane, and methanol + water, respectively, and of Fischer et al., who applied the NPT + test particle method to binary mixtures of methane, ethane, and carbon dioxide [4], and to the ternary methane + ethane + carbon dioxide system [13]. A goal of the aforementioned [4, 6, 9, 10, 13] simulations studies has been to produce effective two - body potentials that can accurately reproduce experimental vapor pressure data for fluids and their mixtures. This goal may be unrealistic because it is likely that three- and higher-body potentials will ultimately be required to accurately calculate the fluid properties from the first principles. In this paper, for mixture PT_{xy} calculations we circumvent the problem of obtaining accurate two-body potentials by means of the incorporation of experimental pure-fluid phase equilibrium data into the mixture phase simulations.

A proposed molecular-based computer simulation technique that is similar in spirit to the GEMC method is the reaction ensemble Monte Carlo (REMC) method for calculating reaction equilibrium compositions, given an intermolecular potential model for the mixture species [14]. This approach incorporates the ideal-gas driving terms for the reactions, $\{\Delta G_j^0(T)\}$, where $\Delta G_j^0(T)$ is the standard-state Gibbs energy change for reaction j . In addition to simple model molecular systems [14] the method has been applied to chemical reactions at the surfaces [15] and to the bulk $\text{Br}_2 + \text{C}_2 + \text{BrCl}$ system [16]. The main goal of this paper is to present a computer simulation method for calculating phase equilibria in multicomponent mixtures. The approach, which is a combination of the GEMC and REMC methods, incorporates knowledge of pure-component vapor-pressure data into the phase equilibrium calculations for the mixtures. Such data are also used by the empirically based thermodynamic methods; however, unlike these approaches, our approach uses no mixture experimental data of any kind. The motivation for the method arises from considering phase equilibrium as a special case of a chemical reaction [17]. We call the approach the reaction Gibbs ensemble Monte Carlo (RGEMC) method. In the following section, we describe the intermolecular potential models used for the species involved. In the subsequent section, we discuss the details of the computer simulations. Subsequent sections discuss the results and present conclusions.

2. The Reaction Gibbs Ensemble Monte Carlo (RGEMC) Method

Vapor pressures, $P_{\text{sat}}(T)$, obtained from pure-fluid GEMC simulations differ from the experimental vapor pressures typically by about 10% [18]. This accuracy is not satisfactory for accurate prediction of the $PTxy$ phase equilibrium properties of mixtures. However, it is well known that the pressure is very sensitive to the form and the parameters of intermolecular potential, whereas other properties are less sensitive [19]. Other workers [10, 20] have attempted to address these inaccuracies by modifying the intermolecular potential parameters of the mixture, in some cases allowing them to be temperature dependent [9]. This is typically a very computationally intensive task. Here, we present an alternative approach to improving the accuracy of mixture phase equilibrium calculations, which is very simple to implement. It relies upon utilizing available information concerning the pure component vapor-pressure data, as are similarly used in the case of the empirically based thermodynamic approaches. The key to the RGEMC approach is to consider phase equilibrium as a *chemical reaction*, a viewpoint often taken by workers concerned with the calculation of combined reaction and phase equilibrium [17].

In the following, we assume that experimental vapor-pressure data are available for the pure-fluid components of the mixture, and that preliminary GEMC simulations have been performed for each pure component using the assumed intermolecular potential model. Then, for the gas phase in equilibrium with the liquid for each pure species, we have for the experimental (exp) and the simulation (GEMC) data, respectively:

$$\mathbf{m}_{i,\text{exp}}^{e,g} = RT \ln f_{i,\text{exp}}^{\text{sat}} \quad (1)$$

$$\mathbf{m}_{i,\text{GEMC}}^{e,g} = RT \ln f_{i,\text{GEMC}}^{\text{sat}} \quad . \quad (2)$$

Where μ_i^e is the excess chemical potential of species i , R is the universal gas constant, f_i is the fugacity of species i , and superscript g denotes the gas phase. Combining the above equations gives

$$\mathbf{m}_{i,\text{exp}}^{e,g} = \mathbf{m}_{i,\text{GEMC}}^{e,g} + RT \ln \left(\frac{f_{i,\text{exp}}^{\text{sat}}}{f_{i,\text{GEMC}}^{\text{sat}}} \right) \quad (3)$$

$$\approx \mathbf{m}_{i,\text{GEMC}}^{e,g} + RT \ln \left(\frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}} \right) \quad , \quad (4)$$

where the last approximation ignores the dependence of the fugacity coefficient ratio on the pressure. Equation (4) is equivalent to writing an accurate total chemical potential of the gaseous species as

$$\mathbf{m}_i^g = \mathbf{m}_i^0(T, P^0) + RT \ln \left(\frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}} \right) + \mathbf{m}_{i,\text{GEMC}}^{e,g} \quad , \quad (5)$$

where $\mu_i^0(T, P^0)$ is the standard chemical potential in the ideal gas state at the reference pressure P^0 [21]. We may combine the first two terms to give

$$\mathbf{m}_i^g = \mathbf{m}_i^{0,*}(T, P^0) + \mathbf{m}_{i,\text{GEMC}}^{e,g}, \quad (6)$$

where, $\mu_i^{0,*}(T, P^0)$ is a modified standard chemical potential given by

$$\mathbf{m}_i^{0,*}(T, P^0) = \mathbf{m}_i^0(T, P^0) + RT \ln \left(\frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}} \right). \quad (7)$$

We now use the REMC method for the mixture, incorporating the chemical-reaction-like term, $\mu_i^{0,*}(T, P^0)$ for each gaseous species. We consider phase equilibrium to result from the “chemical reactions”

$$A_i(g) = A_i(l), \quad (8)$$

where A_i denotes a particular species and l denotes the liquid phase. The phase equilibrium condition is the equality of the chemical potentials of each species in each phase, or equivalently that the total Gibbs energy change vanishes across the reaction. The standard Gibbs energy change for the reaction of eq. (8) is

$$\Delta G_i^0(T) = RT \ln \left(\frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}} \right) \quad (9)$$

The REMC method requires as input an intermolecular potential model and the standard Gibbs energy changes for each reaction i , the latter incorporated in the ideal gas driving term G for the reaction, given by

$$\Gamma_i \equiv \exp \left[\frac{\Delta G_i^0(T)}{RT} \right] = \frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}} \quad (10)$$

By considering the mixture phase equilibrium as resulting from the set of reactions denoted by eq. (8), we might implement the REMC method by utilizing the following transition probability expressions for the transfer of particles between liquid and vapor boxes in the mixture simulation. When the phase equilibrium is treated as the chemical reaction (8), the transition probability $k \rightarrow l$ for the transfer of a particle from a liquid box (l) into a vapor box (g) is

$$P_{kl}^{l \rightarrow g} = \min \left\{ 1, \Gamma_i \exp \left[-\mathbf{b} \Delta U_{kl}^l - \mathbf{b} \Delta U_{kl}^g + \ln \frac{N^l V^g}{(N^g + 1) V^l} \right] \right\}. \quad (11)$$

Similarly, the transition probability $k \rightarrow l$ for the transfer of a particle from a vapor box (g) into a liquid box (l) is

$$P_{kl}^{g \rightarrow l} = \min \left\{ 1, \frac{1}{\Gamma_i} \exp \left[-\beta \Delta U_{kl}^g - \beta \Delta U_{kl}^l + \ln \frac{N^g V^l}{(N^l + 1) V^g} \right] \right\} \quad (12)$$

In eqs. (11) and (12), $\beta = 1/(k_B T)$ and k_B is Boltzmann's constant, $\Delta U_{kl}^a = \Delta U_k^a - \Delta U_l^a$ is the change in configurational energy in box \mathbf{a} , V^a is the volume of box \mathbf{a} , and N^a is the total number of molecules in box \mathbf{a} . In eqs (11) and (12), the ideal-gas driving term G for the phase equilibrium reaction i is given by eq. (10).

3. Intermolecular Potential Models

The two-center Lennard-Jones model of the ethane-type alternative refrigerants consists of two interaction centers at a distance l apart and a point dipole μ in the center of the molecule. The interaction centers interact *via* the Lennard-Jones 12-6 potential. The intermolecular potential for the 2CLJD fluid, u_{2CLJD} , is

$$u_{2CLJD}(r; \mathbf{w}_i; \mathbf{w}_j) = u_{2CLJ}(r; \mathbf{w}_i; \mathbf{w}_j) + u_D(r; \mathbf{w}_i; \mathbf{w}_j) \quad , \quad (13)$$

where r is the distance between centers of mass of molecule j and molecule i , and \mathbf{w}_i ; \mathbf{w}_j is the orientation of molecules. The 2CLJ interaction, u_{2CLJ} , is defined as

$$u_{2CLJ}(r, \mathbf{w}_i, \mathbf{w}_j) = \sum_{a=1}^2 \sum_{b=1}^2 4\mathbf{e} \left[\left(\frac{\mathbf{s}}{r_{ab}} \right)^{12} - \left(\frac{\mathbf{s}}{r_{ab}} \right)^6 \right] \quad (14)$$

In eq. (14), r_{ab} is the distance between atom a of molecule i and atom b of molecule j , \mathbf{e} and \mathbf{s} are the L-J energy and size parameters, respectively. The interaction between two point dipoles μ_i and μ_j , u_D , is given as

$$u_D(r, \mathbf{w}_i, \mathbf{w}_j) = -\mathbf{m}_i \mathbf{T}(\mathbf{r}) \mathbf{m}_j \quad , \quad (15)$$

where $\mathbf{r} = \mathbf{r}_j - \mathbf{r}_i$ is the distance vector between centers of mass of molecules j and i . Dipole-dipole tensor $\mathbf{T}(\mathbf{r})$ is

$$T_{ab} = \frac{3r_a r_b}{r^5} - \frac{\mathbf{d}_{ab}}{r^3} \quad (16)$$

with Kronecker's symbol \mathbf{d}_{ab} . For model fluids, we used the L-J reduced units: $L=l/\mathbf{s}$, $t^* = t/(\mathbf{s}(\mathbf{m}\mathbf{e})^{1/2})$, $T^* = k_B T/\mathbf{e}$, $\mathbf{r}^* = \mathbf{r}\mathbf{s}^3$, $p^* = p\mathbf{s}^3/\mathbf{e}$, $h^* = h/N\mathbf{e}$, $\mathbf{m}^* = \mathbf{m}^2/(4p \in_0 \mathbf{e}\mathbf{s}^3)$

4. Computational Details

The required VLE data for pure fluids were computed by the Gibbs-Duhem

integration [5]. The Gibbs-Duhem integration solves numerically the Clapeyron equation

$$\left(\frac{d \ln p^*}{d(1/T^*)} \right)_s = - \frac{T^*}{p^*} \frac{h_v^* - h_l^*}{1/r_v^* - 1/r_l^*} \quad (17)$$

and evaluates the right-hand side of the Clapeyron equation from molecular simulations. In eq. (17), h_v^* and h_l^* are the vapor and liquid enthalpies respectively, and r_v^* and r_l^* are the vapor and liquid number densities respectively; the subscript s indicates that the derivative is taken along the saturation line. We evaluated the right hand side of the Clapeyron equation by means of constant pressure-constant temperature (NPT) molecular dynamics (MD) simulations [22].

For the binaries, we used the NPT RGEMC and the NPT GEMC simulations to determine the vapor-liquid coexistence curves. The NPT RGEMC and NPT GEMC simulations were organized in cycles as follows. Each cycle consisted of three steps: n_D translational and rotational moves, n_V volume moves, and n_T particle transfers. The three types of moves were selected at random with fixed probabilities, chosen so that the appropriate ratios of each type of move were obtained. The ratio $n_D:n_V:n_T$ in the cycle was set to $N:2:5000$. The initial equilibration period required $0.5-1 \times 10^5$ cycles and final production runs were carried out using $1 - 2 \times 10^5$ cycles.

5. Results and Discussion

5.1 Pure Fluids

VLE data of the 2CLJD fluids were represented by Wagner equations. First of all, we estimated the critical temperature T_c^* and density r_c^* from a least-squares fit of the law of rectilinear diameter

$$\frac{r_l^* + r_v^*}{2} = r_c^* + C_1(T^* - T_c^*) \quad (18)$$

and critical scaling relation

$$r_l^* - r_v^* = C_2(T_c^* - T^*)^{0.325} \quad (19)$$

The fit of eq. (18) was performed over the whole temperature range and that of eq. (19) for temperatures at proximity of expected critical point. Then, vapor pressures p_c^* were fitted to Wagner equation

$$\ln \left(\frac{p_s^*}{p_c^*} \right) = \left(\frac{T_c^*}{T^*} \right) \left(N_{1p}t + N_{2p}t^{3/2} + N_{3p}t^{5/2} + N_{4p}t^5 \right) \quad , \quad (20)$$

where $t = 1 - T^*/T_c^*$. Finally, to correlate coexistence envelopes analytically we

utilized Wagner expressions for description of saturated-liquid densities \mathbf{r}_l^*

$$\ln\left(\frac{\mathbf{r}_l^*}{\mathbf{r}_c^*}\right) = (N_{1l}t^{2/6} + N_{2l}t^{3/6} + N_{3l}t^{7/6} + N_{4l}t^{9/6}) \quad (21)$$

and saturated-vapor densities \mathbf{r}_v^* [22].

$$\ln\left(\frac{\mathbf{r}_v^*}{\mathbf{r}_c^*}\right) = (N_{1v}t^{2/6} + N_{2v}t^{4/6} + N_{3v}t^{7/6} + N_{4v}t^{13/6} + N_{5v}t^{25/6}). \quad (22)$$

The 2CLJD model has four adjustable potential parameters $L=l/s$, \mathbf{e} , \mathbf{s} , and $\mathbf{m}^{*2} = \mathbf{m}^2 / (4p \in_0 \mathbf{e} \mathbf{s}^3)$ that must be fitted to selected experimental data. We fitted \mathbf{e} to the experimental critical temperature and \mathbf{s} to the experimental saturated-liquid density at one temperature (we chose $T = 0.75 T_c$), and we adjusted the dipole moment to the steepness of the vapor pressure curve. We performed the adjustment for both elongations $L = 0.505$ and 0.67 , and allowed dipole moments to be higher than experimental values (to take into account effects of the molecular polarity and angle between the dipole vector and molecular axis). We found that the 2CLJD model with $L = 0.67$ and $\mathbf{m}^{*2} = 7$ represents best the steepness of the vapor-pressure curve for all investigated refrigerants [23]. The derived potential parameters based on this model are listed in Table 1.

We present a comparison between VLE data calculated from the 2CLJD fluid and REFPROP database in Figure 1. For the coexisting densities and vapor pressure. Proclaimed uncertainties of the REFPROP saturated-liquid densities are up to 3%. One can observe from Figure 1 that the agreement between the calculated and REFPROP saturated-liquid densities is excellent for all investigated alternative refrigerants. The calculated saturated- liquid densities lie within the region of experimental uncertainty. As it is seen from Figure 1 the agreement between the calculated and REFPROP vapor pressure is good for the investigated alternative refrigerants. The calculated vapor pressures are systematically higher than REFPROP values.

Table 1: Potential parameters HFC refrigerants

Refrigerant	\mathbf{e}/k_B (K)	\mathbf{s} (Å)	L	l (Å)	\mathbf{m}^{*2}	\mathbf{m} (D)
HFC-32 (CH ₂ F ₂)	199.6	4.007	0	0	1.481	1.62
HFC-134a (CH ₂ FCF ₃)	140.4	3.819	0.67	2.559	7	2.749
HFC-125 (CHF ₂ CH ₃)	127.25	3.898	0.67	2.612	7	2.699

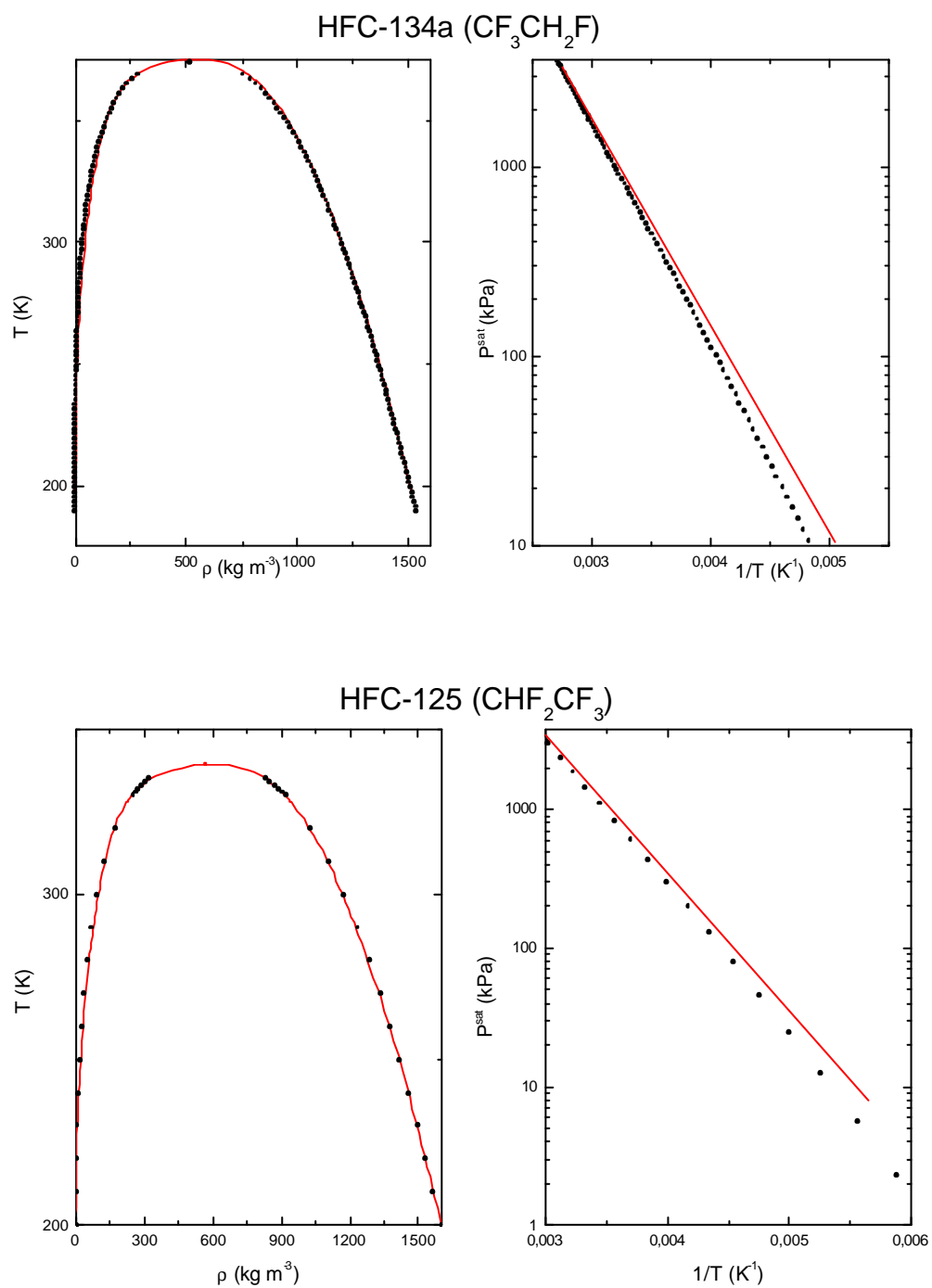


Figure 1: Vapor-liquid equilibria and vapor pressures of hydrofluorocarbon refrigerants. ●, REFPROP; — Gibbs-Duhem integration of 2CLJD liquid

5.2 Binaries

We calculated the VLE behavior for the HFC 125+HFC 134a system and for the HFC 134a+HFC 32 using RGEMC simulations. The Pxy diagrams for these mixtures are shown in Figures 2 and 3 at individual temperatures. In Figure 2, we compare the results from our RGEMC simulations with REFPROP experimental data, and with our predictions using the Wilson and UNIFAC methods for HFC 125+HFC 134a system. For this system, the simulated compositions agree within their statistical uncertainties with the experimental data; the Wilson method also agrees quite well with the experimental values and is slightly better than the UNIFAC method. In Figure 3, we compare the results from our RGEMC simulations with REFPROP experimental data, and with our predictions using the Wilson and UNIFAC methods for HFC 134a+HFC 32 systems. For this system, the simulated compositions agree within their statistical uncertainties with the experimental data. In vapor phase the UNIFAC method results are in very good accord with the experimental results; the Wilson method results are a little bit worse. In liquid phase The Wilson method results are in a very good accord with the experimental results, while UNIFAC method results are in good accord with experimental data.

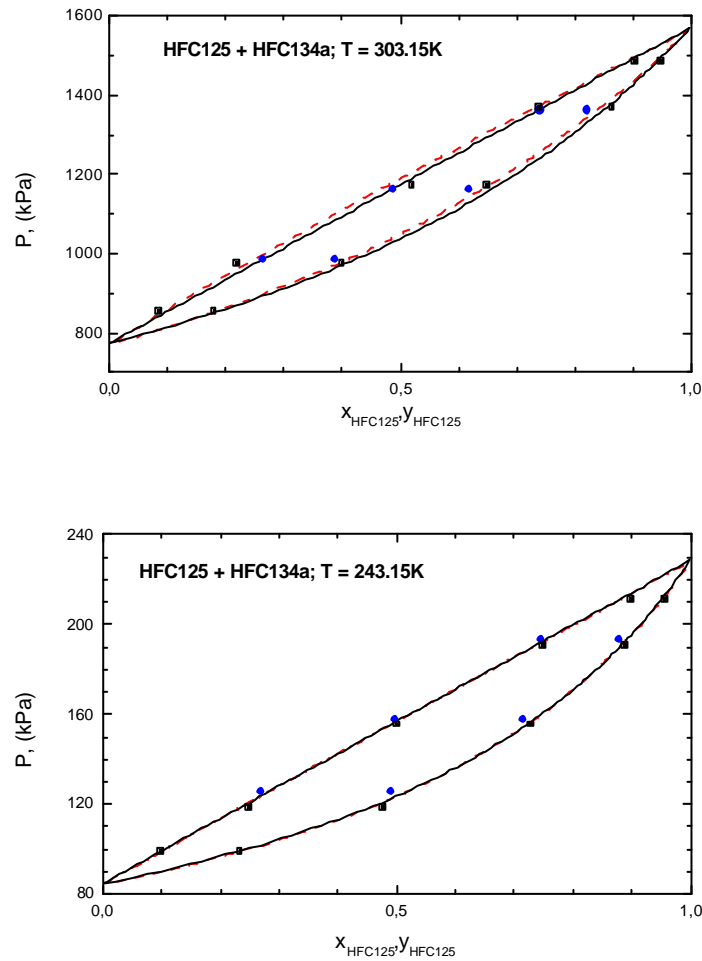


Figure 2: The pressure-composition diagram for the HFC 125+HFC 134a system.
●, REFPROP; ■, RGEMC; —, UNIFAC method; - - -, Wilson method.

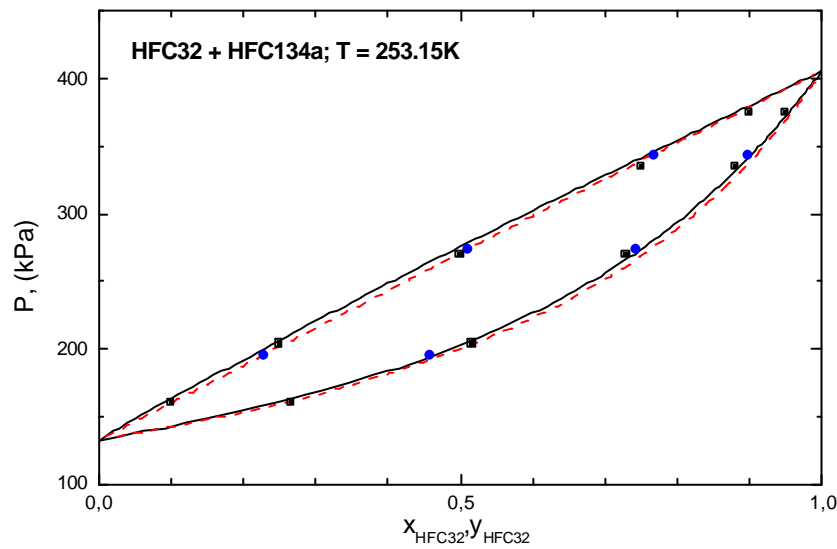
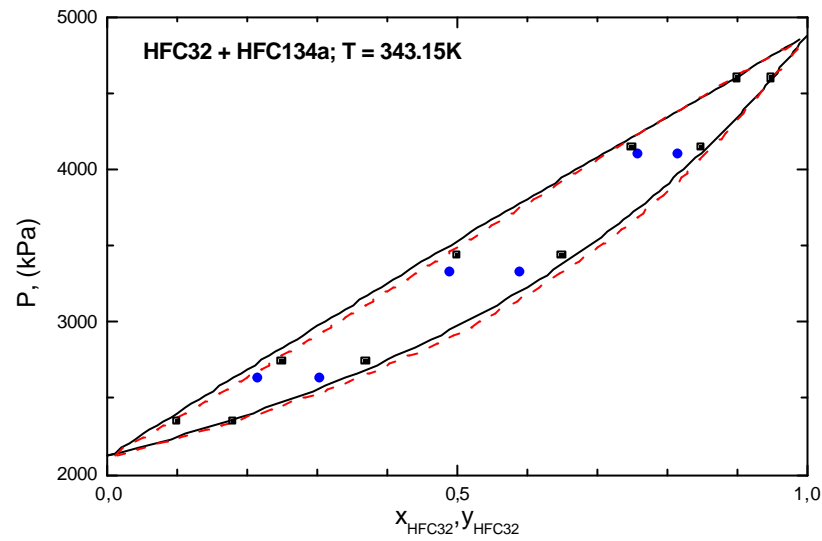


Figure 3: The pressure-composition diagram for the 134a+HFC 32 system.
 ●, REFPROP; ■, RGEMC; —, UNIFAC method; - - -, Wilson method.

6. Conclusions

The dipolar two-center Lennard-Jones fluid to model hydrofluorocarbon refrigerants has been used. We have calculated vapor-liquid equilibrium of the pure fluids and binary mixtures. We have calculated the vapor-liquid equilibrium by Gibbs - Duhem integration for pure fluids. Finally, we have used a method, called the reaction Gibbs ensemble Monte Carlo method, for evaluation of VLE of binaries. This method represents a combination of the Gibbs ensemble Monte Carlo method and the reaction ensemble Monte Carlo method. The approach treats the phase equilibrium conditions

as a special type of chemical reaction and incorporates knowledge of the pure-substance vapor-pressure data into the simulations.

The reaction Gibbs ensemble Monte Carlo method utilizes only an intermolecular potential model and pure-component vapor pressure data. Unlike many thermodynamic-based approaches, no mixture information is required; also (unlike some thermodynamic-based approaches), the mixture volumetric properties are a byproduct of the calculations.

We have used the reaction Gibbs ensemble Monte Carlo method to predict phase equilibrium data of the two binary system, the HFC 125+HFC 134a and HFC 134a+HFC 32. The predictions seem to be excellent, and of comparable accuracy to those obtained using the Wilson and the UNIFAC thermodynamic-based approaches.

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